

PATENT SPECIFICATION

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 7C16C 7C17 7C18 7C20B 7C20C 7C20D1 7C20D2
 7C20D3 7C7 7C8B 7D1A 7D1C 7K4 E2



(54) STABILIZED FILM-FORMING POLYOLEFIN COMPOSITION

(71) We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York, 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the stabilization of thermoplastic polyolefin resin based film forming compositions.

Canadian Patent 758,151 discloses film forming compositions which are useful in the fabrication of synthetic paper. These compositions comprise a thermoplastic polyolefin base resin, such as a high density polyethylene resin, a polymeric accommodation agent such as an ethylene-vinyl acetate copolymer, and various filler materials.

For some commercial applications, these film forming compositions can be used without substantial modification because the properties of the compositions, and/or those of the products made therewith, are not adversely affected by the conditions under which the products are made or used. For some other types of applications, the film forming compositions must be modified by the addition of a single stabilizing agent for the purposes of alleviating an individual problem which arises during the preparation or use of products made with the compositions. United States Patent 3,425,981, for example, discloses the use of ethylene oxide polymers as anti-static agents in film-forming compositions. The patent and technical literature is also replete, of course, with examples of the use of various other types of stabilizing agents such as ultra-violet light (UV) stabilizers and antioxidants

and other thermal stabilizers which are used with film forming compositions. Because of the great number of each of the various types of stabilizing agents which are known to those in the polymeric film forming arts, it is sometimes readily possible to select one of a given type of stabilizing agent, and obtain the desired stabilizing effect with the selected agent. Since only one stabilizing agent is being added to the basic composition in such instances, it is relatively easy to select one agent which will not cause any adverse effects on the physical properties of the final product because of possible chemical or physical incompatibility with the other components of the product, or with the product itself. However, when attempts were made to use the above-described basic film forming compositions for certain commercial applications which require the use of a very high quality product, such as film or paper to be used in the graphic arts field, it was found that the products had to be simultaneously stabilized or protected against several different types of adverse processing or end-use conditions. The difficulty thus presented was not only that of finding a separate stabilizing agent that would provide protection against each of the different types of adverse use conditions, but that each of these stabilizing agents, which are each highly complex chemical compounds, had to be functionally and chemically compatible, not only with the components of the basic film formulation, but also with each other and with the final product.

Specifically, it was found that if the polyolefin resin based synthetic paper-like film was to successfully compete with the long established wood-pulp paper products, for use in the graphic arts field as printable plastic film and sheet, the synthetic paper-like film composition had to be simultaneously protected against a

plurality of adverse manufacturing or use conditions so as to provide a useful product having all of the following characteristics:

1) *No Loss of Properties from Heating Aging* — The sheet must pass the Book Manufacturers Institute (BMI) specification of no change in properties after exposure to 105° C. for 24 hours. This means effective stabilization against embrittlement due to oxidative molecular chain scission.

2) *No Surface or Visual Defects* due to "melt fracture" or "orange peel". These develop during the plastic extrusion or equivalent sheet manufacturing process as a result of inadequate stabilization against oxidative molecular crosslinking.

3) *High Rate of Static Dissipation*. This is required for use with high speed printing presses. Plastics have notoriously poor dissipation and require very specific and effective anti-static additives.

4) *Stability Against Ultra-Violet Light Degradation*. Graphic art materials must be used outdoors and under fluorescent lighting. Polyolefins have inherently poor stability and require very specific and effective stabilizers to retard embrittlement and color change.

5) *No Loss of Glue or Ink Properties*. The various additives, stabilizers and other components must not initially interfere with drying ability or adhesion and must not migrate or bleed out with time or heat.

6) *No Color Change*. The sheet must not lose whiteness or develop colours with the passage of time or under heat or light conditions.

Accordingly the present invention provides a polyolefin composition comprising a polyolefin and stabilizingly effective quantities of: an ultra-violet light stabilizer which comprises at least one organic compound having a chemical structure such that it is capable of forming a six membered chelate ring through hydrogen bonding, the compound being a solid or liquid which does not decompose or volatilize below 200° C; an anti-static agent which comprises at least one alkoxylated amine or amide which contains at least one saturated or unsaturated hydrocarbon group having from 7 to 22 carbon atoms and optionally bearing one or more substituents, and which does not volatilize or decompose below 200° C; and a thermal stabilizer which comprises at least one sterically hindered phenol which does not volatilize or decompose below 200° C.

The invention also provides a process which comprises preparing a paper-like film from a polyolefin composition comprising a polyolefin and stabilizingly effective quantities of: an ultra-violet light stabilizer which comprises at least one organic compound which does not volatilize or decompose below 200° C and is a 2-hydroxy-benzophenone or 2-hydroxyphenyl-benzotriazole derivative of the formulae given below; an anti-static agent

which comprises at least one compound which does not volatilize or decompose below 200° C and is an alkoxylated amide or amine which contains at least one saturated or unsaturated hydrocarbon group having from 7 to 22 carbon atoms and optionally bearing one or more substituents; and a thermal stabilizer which is at least one sterically hindered phenol which does not volatilize or decompose below 200° C.

The object of the present invention is to provide a polyolefin resin based film forming composition which attempts to provide the above described characteristics of paper which is useful in the graphic arts field.

It has now been found that the object of the present invention may be provided by a film forming composition which comprises:

45 to 85, and preferably 65 \pm 2, weight per cent of high density polyethylene or polypropylene as the base thermoplastic resin,

5 to 45, and preferably 28 \pm 5, weight per cent of filler,

3 to 15, and preferably 6 \pm 1, weight per cent of polymeric accommodation resin,

0.1 to 2.0, and preferably 0.18 \pm 0.03, weight per cent of the anti-static agent,

0.2 to 2.0, and preferably 0.5 \pm 0.1, weight per cent of the UV stabilizer, and,

0.02 to 1.0, and preferably 0.07 \pm 0.03, weight per cent of the thermal stabilizer,

with the understanding that the selection of the weight per cents of the individual components is such that the total weight per cent amounts to 100. A preferred formulation to be used in this regard, therefore, is one of the following composition, wherein all three of the different types of stabilizing or protective agents are employed:

| Component | Weight % | |
|---------------------|----------|-----|
| Base resin | 65.25 | 105 |
| Accommodation resin | 6.00 | |
| Filler | 28.00 | |
| UV stabilizer | 0.50 | |
| Anti-static agent | 0.18 | 110 |
| Thermal stabilizer | 0.07 | |
| | 100.00 | |

Base Resin

The base resin is preferably a solid (at 25° C.) thermoplastic polyolefin resin which is preferably high density polyethylene and/or polypropylene.

The high density polyethylene resins useful as the base resins in the present invention are essentially linear in structure, and are known The terms "high density" or "linear polyethylene resins can and usually do contain chain transfer agents, and/or chain terminating agents to modify the melt viscosity, molecular weights and other properties of the resins. The terms "high density" or "linear polyethylene" are intended to encompass polymers

containing such agents as integral units of the polymer.

The high density polyethylenes are generally characterized by a density of about ≥ 0.94 , and usually in the range of from 0.94 to about 0.97.

The high density polyethylene resins useful in the present compositions exhibit a melt index of from 0.005 to 5.0 and preferably from 0.15 to 0.5 decigrams per minute.

It should be noted, however, that mixtures of high density polyethylene resins can be used as the base resin in the present compositions, and in such mixtures polyethylene resins which exhibit a melt index less than 0.005 or greater than 5.0 decigrams per minute can be used provided the melt index of the polyolefin base resin mixture is from 0.005 to 5.0 and preferably from 0.15 to 0.5 decigrams per minute.

The polypropylene used in the base resin can be any of the solid forms of polypropylene, and preferably those having a melt flow of from about 0.01 to about 4.5 decigrams per minute and a density of >0.90 and preferably of >0.91 to <0.92 .

The base resin can consist entirely of either the high density polyethylene resin or the polypropylene resin, or it can comprise a mixture of these two polyolefin resins.

Polymeric Accommodation Resin

The polymeric accommodation resin is a solid material (at 25°C.) which is capable of wetting the particles of filler material so as to facilitate the homogeneous dispersion of the filler materials in the final products and the accommodation resin must be miscible with, i.e., physically compatible with the base resin. The accommodation resin has different flow properties than those of the base resin. The accommodation resin may be a low density homopolymer or ethylene, or a copolymer of ethylene with one or more comonomers, or a mixture of the low density homopolymer and the copolymer, or any other organic polymer having the desired functional properties. The preferred accommodation resin is the low density homopolymer of ethylene.

The low density ethylene homopolymers have densities of <0.94 , and usually in the range 0.91 to 0.93. The low density ethylene homopolymers have melt indices of 0.2 to 100 inclusive, and preferably from 0.5 to 20 inclusive, decigrams minute.

The ethylene copolymers comprise ethylene and one or more other monomers, such as vinyl monomers, which are copolymerizable therewith. The copolymerizable vinyl mono-

mers are those containing the $-\text{C}=\text{C}-$ group which can be copolymerized with the ethylene monomer to form thermoplastic copolymers. Illustrative of such vinyl monomers are unsub-

stituted olefins including monoolefins such as propylene, 1-butene; isobutene, and β -pentene; halogenated olefins such as chloroprene, tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropylene; vinyl aryls such as styrene, *o*-methoxystyrene, *p*-methoxystyrene, *m*-methoxystyrene, *o*-nitrostyrene, *p*-nitrostyrene, *o*-methylstyrene, *p*-methylstyrene, *m*-methylstyrene, *p*-phenylstyrene, *o*-phenylstyrene, *m*-phenylstyrene and vinyl-naphthalene; vinyl and vinylidene halides, such as vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride and vinylidene bromide; vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl chloroacetate, vinyl chloropropionate, vinyl benzoate and vinyl chlorobenzoate; acrylic and α -alkyl acrylic acids, their alkyl esters, their amides and their nitriles such as acrylic acid, chloroacrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, *n*-octyl acrylate, 2-ethylhexyl acrylate, *n*-decyl acrylate, methyl methacrylate, butyl methacrylate, methyl ethacrylate, ethyl ethacrylate, acrylamide, *N*-methyl-acrylamide, *N,N*-dimethyl-acrylamide, methacrylamide, *N*-methyl-methacrylamide, *N,N*-dimethyl-methacrylamide, acrylonitrile, chloroacrylonitrile, methacrylonitrile and ethacrylonitrile; maleic and fumaric acid and their anhydrides and alkyl esters such as maleic anhydride, dimethyl maleate and diethyl maleate; vinyl alkyl ethers and ketones such as vinyl methyl ether, vinyl ethyl ether, vinyl isobutyl ether, 2-chloroethyl vinyl ether, methyl vinyl ketone, ethyl vinyl ketone and isobutyl vinyl ketone; also vinylpyridine, *N*-vinylcarbazole, *N*-vinylpyrrolidine, ethyl methylene malonate, acrolein, vinyl alcohol, vinyl acetate and vinyl butyral. Non-vinyl monomers which may be copolymerized with ethylene include carbon monoxide and formaldehyde.

The ethylene copolymers useful in the compositions of the present invention are thermoplastic copolymer resins which exhibit a melt index of from 0.2 to 100 inclusive and preferably from 0.5 to 20 inclusive.

These copolymer resins should contain a predominant amount of the ethylene polymerized in the copolymer. Preferably the copolymer should contain from about 70 to about 95 weight per cent polymerized ethylene monomer.

Preferred copolymer accommodation resins are ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, ethylene/styrene copolymer, ethylene/acrylic acid copolymer and ethylene/propylene copolymers.

The Fillers

The fillers which may be used in the present invention include all those which are commonly employed in thermoplastic resin based synthetic paper. They are preferably used in the

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form of discrete particles having an average particle diameter of from about 0.1 microns to about 15 microns. The filler particles are thus of a non-colloidal size and accordingly contribute to sheet or film, formed from the composition of the invention, a considerable degree of opacity, machineability, surface texture, writeability and printability.

The preferred fillers include the inert metallic oxides, carbonates and sulfates of metals found, for example, in Groups II and IV of the Periodic Table. Illustrative of such fillers are calcium oxide, zinc oxide, magnesium carbonate, calcium sulfate, magnesium sulfate and lead sulfate.

Fillers such as zinc oxide, titanium dioxide, magnesium oxide, and calcium carbonate or mixtures thereof are highly desirable as whiteners if high opaque paperlike films are desired.

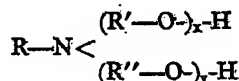
Siliceous fillers such as diatomaceous earths, commercial silicas, silicates, silica gels, silica-aluminas and asbestos, preferably the short fiber asbestos may also be used. It is preferred that the siliceous filler material have an average particle diameter of from 0.5 to 10 microns inclusive.

The preferred filler is calcium carbonate, alone, or in combination with titanium dioxide because of the white color that may be obtained therewith, for a white paper-like film.

Anti-Static Agent

The anti-static agent to be used in the present invention is a solid or liquid material which does not volatilize or decompose below 200° C., and which is an alkoxyated amine or amide which contains at least one C₁ to C₂₂ saturated or unsaturated hydrocarbon group. These compounds may have one of the three structures

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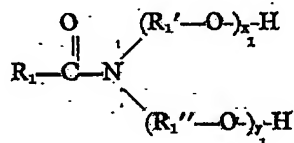


wherein R is a C₈ to C₂₂, inclusive, hydrocarbon radical, saturated or unsaturated,

R' and R'' may be the same or different and are lower alkylene radicals, i.e., C₁ to C₆ inclusive, and

x and y are the same or different whole numbers and each is 1 to 14 inclusive, and the sum of x+y is a whole number from 2 to 15, and preferably 2 to 5 inclusive,

II

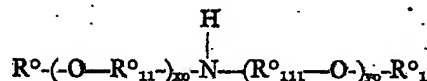


wherein R₁ is a C₇ to C₂₁, inclusive, hydrocarbon radical, saturated or unsaturated,

R₁' and R₁'' may be the same or different and are lower alkylene radicals, i.e., C₁ to C₆ inclusive, and

x₁ and y₁ are the same or different whole numbers and each is 1 to 14 inclusive, and the sum of x₁+y₁ is a whole number from 2 to 15, and preferably 2 to 5 inclusive,

III



wherein R^o and R^o₁ are the same or different and each is H or a C₈ to C₂₂, inclusive, hydrocarbon radical, saturated or unsaturated, with the proviso that not more than one of R^o and R^o₁ is H,

R^o₁₁ and R^o₁₁₁ are the same or different, and are lower alkylene radicals, i.e., C₁ to C₆ inclusive, and

x₀ and y₀ may be the same or different whole numbers and each is 1 to 14 inclusive, and the sum of x₀+y₀ is a whole number from 2 to 15, and preferably about 2 to 5 inclusive.

Specific classes of such anti-static agents are N,N - bis(Z - hydroxyethyl) C₈-C₂₂ alkyl amines, N,N - bis(2 - hydroxyethyl) C₈-C₂₂ fatty acid amides, N,N - bis(3 - hydroxypropyl) C₈-C₂₂ alkylamines, N,N - bis(3 - hydroxypropyl) C₈-C₂₂ fatty acid amides, and N - (C₈-C₂₂ alkoxy - C₁₋₆ alkyl) - alkanolamines.

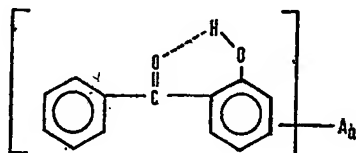
The hydrocarbon and alkylene radicals in the anti-static agents may be substituted with substituents which do not interfere with the intended utility of such agent, such as hydroxyl groups.

The preferred of the anti-static agents is N - (3 - dodecyl - oxy - 2 - hydroxypropyl) - ethanolamine because it is the most thermally stable and provides the most consistent results in terms of range of its effective term of use, i.e., quarter life range.

Ultra Violet Light Stabilizer

The ultra violet light stabilizer to be used in the present invention is a solid or liquid which does not volatilize or decompose below 200° C. and which has a chemical structure such that it is capable of forming a six membered chelate ring through hydrogen bonding. The preferred of such compounds are those which are 2 - hydroxy - benzophenone or 2 - hydroxy - benzotriazole derivatives.

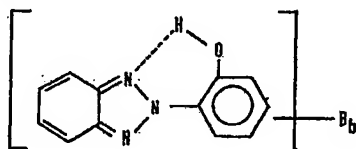
The benzophenone derivatives will have the structure



wherein A represents hydrogen or one or more of the same or different hydrocarbon or hydrocarbonoxy radicals which are substituents on the benzene rings and is or are of such molecular weight as to make the ultra violet stabilizer compound one which does not volatilize or decompose below 200° C., and a is a whole number from 1 to 9 inclusive. The benzophenone derivatives may contain inert substituents other than the hydrocarbon or hydrocarbonoxy radicals which do not interfere with the intended utility of the ultra violet stabilizer such as hydroxy or chlorine radicals.

A specific example of the benzophenone derivative compounds is 2 - hydroxy - 4 - n-octoxybenzophenone.

The benzotriazole derivatives will have the structure



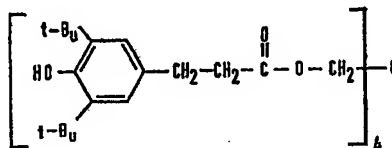
wherein B represents hydrogen or one or more of the same or different hydrocarbon or hydrocarbonoxy radicals which are substituents on the benzene rings and is or are of such molecular weight as to make the ultra violet stabilizer compound one which does not volatilize or decompose below 200° C., and b is a whole number from 1 to 8 inclusive. The benzotriazole derivatives may also contain inert substituents other than the hydrocarbon or hydrocarbonoxy radicals which do not interfere with the intended utility of the ultra violet stabilizer such as hydroxyl or chlorine radicals.

A specific example of the benzotriazole derivatives is 2 - (3,5 - ditertiary butyl - 2-hydroxyphenyl) - 5 - chlorobenzotriazole.

Thermal Stabilizer

The thermal stabilizers to be used in the present invention are solid or liquid materials which do not volatilize or decompose below about 200° C and which are sterically hindered phenols.

Specific examples of such sterically hindered phenols are octadecyl 3 - (3,5 - di - tertiary butyl - 4 - hydroxyphenyl) - propionate and tetrakis 3 - (3,5 - di - tertiary butyl - 4 - hydroxyphenyl) - propionate methylene methane of the formula:—



Additives such as flame retardants and coloring materials can be present in the compositions as well as the stabilizing additives discussed above.

Paper-like films are generally prepared from the compositions of this invention by hot compounding the ingredients at a temperature of from 120° to 200° C in a suitable blending device, rolling the hot blended composition on a two-roll mill or similar device and then cutting the rolled sheet into convenient form or pelletizing. The cut or pelleted material is then charged to an extruder heated to a suitable extrusion temperature and extruded through a film forming die.

Film prepared from the compositions of the present invention can be of any practical thickness. Generally such films are prepared in thicknesses of from about 0.25 to about 20 mils in thickness although films having a thickness of from 2 to 8 mils are preferred.

These films are preferably given surface treatment to impart printability to the surface of the film. Surface treatment means are identical to those used for polyolefin film and include electrostatic discharge such as corona discharge, flame treatment and oxidative chemical treatment. After such surface treatment, the paper-like films of the present invention can be printed with ink compositions normally used for polyolefin films. The films, treated or untreated, can be written upon with pencil and/or ball point pen and subsequently be erased an unlimited number of times with little adverse effect upon the film. This feature makes these films ideal for such products as maps, charts, textbooks, children's books and the like.

The films of this invention, as has been indicated, exhibit characteristic paper-like properties. They are stiff and can be creased to a dead fold, and the surfaces can be finished on a low gloss, matte finish or a high gloss finish. After suitable treatment as discussed above, they can be glued to form laminates or folded to form products and can be printed or written upon. In addition, the films of this invention exhibit characteristic properties which make

them superior to paper, for example, they are both water proof and grease proof, they exhibit superior tensile strength, impact strength and tear resistance, and they can be heat sealed.

5 These features additionally make these films ideal for such uses as hard or flexible book covers, magazine covers, pages for books, magazines and other publications, maps, charts, cards, including greeting cards, catalogue
10 cards, playing cards and the like; currency, bonds, stock certificates and the like; litho plate masking paper; tags, labels and the like; business forms; sheets for photocopies, posters and billboards; wallpaper, packaging, corrugated board, artists and engineering drawing
15 papers including blueprint paper; tracing and white print masters, loose-leaf binders and protective covers, book jackets and the like; window shades, acoustical ceiling covers; wallboard cover; pressure sensitive protective paper,
20 printed tape, shelf paper, patterns, such as dress patterns and the like; record covers and other uses for which paper, paperboard, cardboard and the like will serve.

25 The various physical properties which are reported herein were determined by the following procedures, unless otherwise noted:

Melt index —ASTM—D—1238—62T
Elongation —ASTM—D—882—61T
30 Elmendorf
Tear Resis-
tance —ASTM—D—689—44
Folding
Test—ASTM—D—643—43

35 *Exposure to Ultra Violet light* — sheet is placed 4 inches from a 40 watt fluorescent sun lamp and exposed to the light for the desired testing time.

40 The electrostatic decay rate of a sample is measured in terms of its quarter life, that is the time required in seconds for the loss of 1/4 of the initial induced electric static charge on a Victoreen electrostatic paper analyzer at 74°F. and 46—47% relative humidity,
45 starting with the same initial charge in each case. The sheet is preconditioned for at least 24 hours at 74°F. and 46—47% relative humidity. The equipment is operated at 2000 volts for a 5—7 mil sheet. A dynamic mode
50 test procedure is employed.

In the following Examples, Examples 4, 16, 17, 24, 25, 26, 32 (in part) and 33 (in part) further describe the present invention and are not intended as a limitation
55 upon the scope thereof. The remaining Examples are given for the purpose of comparison.

In the Examples various film forming com-

positions were prepared to illustrate the present invention. In these compositions the base resin used was a high density polyethylene resin having a density of 0.96 and a melt index (MI) of 0.18 decigrams per minute. The accommodation resin used was either a low density polyethylene resin having a density of 0.918 and a MI of 2.0 decigrams per minute or a copolymer containing 80 weight per cent of ethylene and 20 weight per cent of vinyl acetate and having a density of 0.94 and a MI of 2.5 decigrams per minute. The accommodation resins were interchangeable, since the same basic results are obtained with each of the two accommodation resins.

70 The filler used was a combination of calcium carbonate having an average particle diameter of about 0.5 microns, and titanium dioxide having an average particle diameter of about 0.25—0.30 microns.

The compositions evaluated contained 65±2 weight per cent of the base resin, 6 weight per cent of the accommodation resin, 20 weight per cent of calcium carbonate, 8 weight per cent of titanium dioxide, and additional quantities of the various stabilizers, as noted below, to provide a final composition in which the total weight per cent of all of the components thereof amounted to 100.

For each formulation the ingredients were charged to a Banbury type mixer set to reach a compound temperature of 155±5°C in a period of about 2 1/2 minutes and thereafter charged to a two-roll mill and sheeted off. The resultant sheets were pelletized for convenience of handling. The pelletized formulations were converted to film by charging the pellets to a heated, screw type extruder set for a temperature of 200°C. and extruding the molten formulation through an annular tubular film extrusion die followed by expansion by a blown tubular process to form 5 to 7 mil thick films or sheets. Each of the films was stiff and paper-like and could be written upon by both pencil and ball point and erased. The films were then evaluated for other physical properties.

Examples 1—4.

Four formulations were prepared and fabricated into 5 mil thick films or sheets of synthetic paper as described above. Various combinations of anti-static agent, ultra violet stabilizers and thermal stabilizers were used in these formulations, as noted below in Table I. Table I also lists various physical properties of the paper when it was tested for such properties either when the paper was first made, or after the paper had been exposed to the ultra violet light aging test, or a heat aging test (24 hours at 105°C.).

The protective agents evaluated in these Examples were:

5 A—an alkylated aryl phosphite thermal stabilizer sold commercially as Polygard by Naugatuck Chemical Division of U.S. Rubber Co. Polygard is a Registered Trade Mark.

B—tetrakis [3 - (3¹, 5¹ - di - tertiary butyl-

4¹ - hydroxyphenyl) - propionate methyl-ene]methane.

C—polyethylene oxide having a molecular weight of about 850,000 (viscosity of 16,000—32,000 centipoises at 25°C. as a 5% aqueous solution)

D—N - (3 - dodecyloxy - 2 - hydroxypropyl)-ethanolamine

E—2 - hydroxy - 4 - n - octoxybenzophenone

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TABLE I

| | Formulation—% by weight | | | |
|---|-------------------------|--------|--------|--------|
| | 1 | 2 | 3 | 4 |
| Protective Agent | | | | |
| Thermal stabilizer | A—0.07 | B—0.07 | B—0.07 | B—0.07 |
| Anti-static agent | C—2.0 | C—2.0 | D—0.18 | D—0.18 |
| Ultra Violet stabilizer | — | — | — | E—0.50 |
| Physical Properties | | | | |
| 1. Ultimate elongation(%) | | | | |
| a) original value | 910 | 865 | 797 | 923 |
| b) after heat aging | 0 | 870 | 868 | 951 |
| c) after ultra violet exposure— days to failure | 8 | 8 | 14 | >40 |
| 2. Elmendorf Tear Resistance (grams/mil) | 44 | 40 | 34 | 38 |
| 3. Number of folds to break— | | | | |
| a) original values | 24,652 | 34,223 | 68,209 | 36,850 |
| b) after ultra violet exposure— for 20 days | 39 | 295 | — | 31,477 |
| 4. Printing—in stack drying time—hours | 1—3 | 1—3 | 1—3 | 1—3 |
| 5. Static decay $\frac{1}{2}$ life rate (seconds) (dynamic mode) | >60 | >60 | <1 | <1 |

20 The test results shown in Table I demonstrate that, of the formulations evaluated, only the formulation which is stabilized in accordance with the present invention, i.e., formulation 4, provides a synthetic paper-like film having all the necessary qualities of

25 graphic arts paper. Formulations 1 and 2, which contain a prior art antistatic agent, polyethylene oxide, do not have the anti-static properties required for use on the high speed printing presses which are commonly used in the graphic arts field today. The Polygard thermal stabilizer also does not provide the necessary thermal stability. A paper-like film made with the Polygard stabilizer also shows severe orange peel imperfections. Formulation 3 does not have the necessary degree of ultra violet protection.

Examples 5—17.

Various formulations were prepared in which only the thermal stabilizer was changed. Example 5 is a control in which no thermal stabilizer was used, and Examples 6—17 represent samples in which an individual thermal stabilizer, or a combination of thermal stabilizers, was used at a total level of 0.07% by weight. The thermal stabilizers employed, and the physical properties of the paper-like film made therewith are shown below in Table II. 5 Mil thick paper-like film made for each of the Examples was formulated and prepared as noted above. The physical values shown are obtained with the use of the combination of the UV stabilizer and anti-static agent of the present invention.

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TABLE II

| Example | Heat Stabilizer | Melt Index (% Drop After 30 min. on 200°C. Roll-Mill) Compound | Color Compound | Orange Peel (Melt Fracture) Sheet | % of Original Elongation After 5 Days @ 105°C. Sheet | Ink Drying (In Stack) Sheet |
|---------|---|--|-------------------|---|--|-----------------------------------|
| 5 | None | 100 | — | — | | |
| 6 | Dibutylparacresol (DBPC) | 100 | Yellow | — | | |
| 7 | Polygard | 79 | None | Seytre | 0 | 2—3 hr. |
| 8 | Distearylthiodipropionate (DSTDP) | 74 | None | | | |
| 9 | 50/50 DBPC/Polygard | 89 | Yellow | | | |
| 10 | 50/50 DSTDP/Polygard | 100 | None | | | |
| 11 | Tris (2-Methyl-4-Hydroxy-5-Tertiary-Butyl-Phenol) Butane (TMBPB) | 28 | Yellow | | | |
| 12 | 50/50 DBPC/DSTDP | 85 | Yellow | | | |
| 13 | 50/50 TMBPB/Polygard | 100 | Yellow | | | |
| 14 | Phenothiazine | 51 | Pink | | | |
| 15 | 50/50 DBPC/Dilaurylthiodipropionate | — | Yellow | Severe | 0 | > 7 days |
| 16 | Octadecyl 3-(3,5-Di-Tert-Butyl-4-Hydroxyphenyl)-Propionate | 0 | None | | | |
| 17 | Tetrakis [3-(3,5-Di-Tert-Butyl-4-Hydroxyphenyl)-Propionate methylene] Methane | 0 | None | None | 100 | 2—3 hr. |

The test results shown in Table II indicate that it is only with the thermal stabilizers of the present invention, i.e., those employed in Examples 16 and 17, is it possible to obtain the desired combination of physical properties for a graphic arts paper-like film. With the other thermal stabilizers evaluated, the paper loses its physical properties as evidenced by a loss in melt index or loss in % elongation. Various of the stabilizers of Examples 6—15 also provided a paper-like film which was discolored, or showed severe orange peel type surface, or had poor ink drying properties. The orange peel phenomenon is associated with a change in the molecular structure of the base resin during processing of the paper product, as also indicated by a drop in the melt index of the compound. This drop is

attributed to inadequate stabilization against thermooxidative crosslinking.

Examples 18—26

Various formulations were prepared in which only the anti-static agent was changed. Examples 19—26 thus represent formulations in which an individual anti-static agent was used at a level of 0.18 weight %. The various anti-static agents employed, and the physical properties of the paper-like film made therewith are shown below in Table III. 5 and 7 mil thick paper-like film made for each of the Examples was formulated and prepared as noted above. The physical values shown are obtained with the use of the combination of the ultra violet stabilizer and thermal stabilizer of the present invention. In Example 18, 2 weight per cent of the anti-static agent was used.

TABLE III

Electrostatic Decay Rate Quarter Life, sec.
(Dynamic Mode)

| Antistatic Agent | (Average) 7 mil Sheet | (Range) 5 mil Sheet | After Processing 7 min. to 210°C | Color Sheet |
|---|--------------------------|------------------------|-------------------------------------|---|
| | | | (Average) 7 mil Sheet | |
| 18 Polyethylene Oxide | > 60 | | | |
| 19 Lauryl Sarcosyl | > 60 | | | |
| 20 Imidazelen | > 60 | | | |
| 21 Phosphated Mono-Glyceride | > 60 | | | |
| 22 P-Propyleneglycol Mono Stearate | > 60 | | | |
| 23 Quat. Ammonium fatty acid | 3 | | | Lemon color after few days in subdued light |
| 24 N,N-Bis(2-Hydroxyethyl) C ₁₆ —C ₁₈ Alkyl Amine | 35 | | 16 | |
| 25 N,N-Bis(2-Hydroxyethyl) C ₁₈ —C ₁₄ Alkyl Amine | < 1 | 4—> 60 | 8 | |
| 26 N-(3-Dodecyloxy-2-Hydroxy Propyl)-Ethanolamine | < 1 | 2— 8 | 1 | |

The test results shown in Table III indicate that it is only with the anti-static agents of the present invention, i.e., those employed in Examples 24—26, is it possible to obtain the desired combination of physical properties for a graphic arts paper-like film. With the other anti-static agents evaluated the paper-like film had poor anti-static properties or the paper discolored.

Examples 27—33.

Various formulations were prepared in which the use of various ultra-violet light stabilizers

was evaluated in combination with various anti-static agents. Example 27 represents formulations in which no ultra-violet light stabilizer was used, and Examples 28—33 represent formulations in which different ultra-violet light stabilizers were used. Each of the ultra-violet light stabilizers of Examples 28—33, and the control formulation of Example 27, were separately evaluated in combination with each of three anti-static agents, polyethylene oxide, an N,N - bis(2 - hydroxy ethyl) C₁₆—C₁₈ alkylamine, which is listed in

the test combinations was formulated and prepared as noted above. The physical values shown in Table IV are obtained with the use of the thermal stabilizers of the present invention. The elongation tests were run to show the effectiveness of the UV stabilizer. Acceptable plastic paper products should pass the elongation test for at least 25 days of continuous UV lamp exposure as described above.

TABLE IV

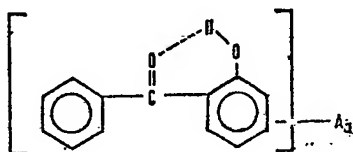
| Example | U.V. Agent | With Polyethylene oxide | | | With AA-1 | | | With AA-2 | | |
|---------|---|----------------------------|--|----------------------------|----------------------------|--|----------------------------|----------------------------|--|----------------------------|
| | | Days to Elongation Failure | Quarter Life Electrostatic Decay Rate, sec. (Dynamic Mode) | Days to Elongation Failure | Days to Elongation Failure | Quarter Life Electrostatic Decay Rate, sec. (Dynamic Mode) | Days to Elongation Failure | Days to Elongation Failure | Quarter Life Electrostatic Decay Rate, sec. (Dynamic Mode) | Days to Elongation Failure |
| 27 | None | > 5 < 14 | > 60 | > 18 < 23 | 14 | > 14 < 18 | < 1 | | | |
| 28 | 4 T-Butyl Phenyl Salicylate | > 8 < 10 | — | — | — | — | — | — | — | — |
| 29 | Zinc Oxide (8%) | — | — | — | — | > 10 < 15 | — | — | — | — |
| 30 | 2,2'-Thio-Bis(4-T-Octylphenolate)Nickel (II) | — | — | — | — | > 10 < 14 | > 60 | > 10 < 14 | > 60 | > 60 |
| 31 | 2,2'-Thio-Bis(4-T-Octylphenolate)-N-Butyl-amine Nickel (II) | > 35 | < 60 | > 26 < 30 | > 60 | > 40 | > 60 | > 40 | > 60 | > 60 |
| 32 | 2-Hydroxy-4-n-Octoxy Benzophenone | > 8 < 10 | > 60 | — | — | > 40 | < 1 | > 40 | < 1 | < 1 |
| 33 | 2-(3',5'-Ditert-Butyl-2'-Hydroxy-Phenyl)-5-chloro-Benzotriazole | — | — | — | — | > 40 | 6 | > 40 | 6 | 6 |

The test results shown in Table IV indicate that it is only when the UV stabilizers of the present invention are used in combination with the anti-static agents of the present invention, i.e., the use of the UV stabilizers of Examples 32 and 33 with anti-static agents AA-1 and AA-2, it is possible to provide the desired combination of physical properties for a graphic arts paper-like film. The other combinations of UV stabilizer and anti-static agent provided a paper-like film which had poor electrostatic decay properties and/or the elongation of such a paper-like film failed within a short time. The test results of the Example 31 series of experiments indicates further that a negative synergistic effect on the electrostatic decay life of the paper was in fact obtained by the use of the anti-static agents of the present invention with the organonickel UV stabilizer with which they were combined.

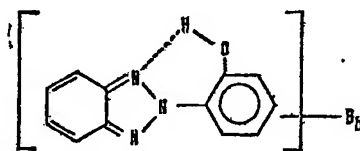
WHAT WE CLAIM IS:—

1. A polyolefin composition comprising a polyolefin and stabilizingly effective quantities of: an ultra-violet light stabilizer which comprises at least one organic compound having a chemical structure such that it is capable of forming a six membered chelate ring through hydrogen bonding, the compound being a solid or liquid which does not decompose or volatilize below 200°C; an anti-static agent which comprises at least one alkoxyated amine or amide which contains at least one saturated or unsaturated hydrocarbon group having from 7 to 22 carbon atoms and optionally bearing one or more substituents, and which does not volatilize or decompose below 200°C; and a thermal stabilizer which comprises at least one sterically hindered phenol which does not volatilize or decompose below 200°C.

2. A composition as claimed in claim 1 wherein the ultra-violet light stabilizer comprises at least one compound which has either the structure



wherein A represents hydrogen or one or more of the same or different substituted or unsubstituted hydrocarbon or hydrocarbonoxy, hydroxyl or chlorine radicals substituted on the benzene rings of such a benzophenone compound, and α is a whole number from 1 to 9 inclusive; or the structure:—

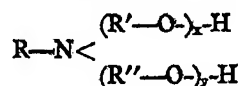


wherein B represents hydrogen or one or more of the same or different substituted or unsubstituted hydrocarbon or hydrocarbonoxy, hydroxyl or chlorine radicals substituted on the benzene rings of such a benzotriazole compound and b is a whole number of 1 to 8 inclusive.

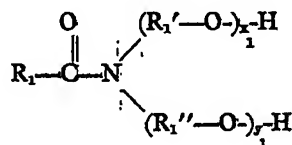
3. A composition as claimed in claim 2 wherein the ultra-violet light stabilizer is 2-hydroxy - 4 - n - octoxybenzophenone.

4. A composition as claimed in claim 2 wherein the ultra-violet stabilizer is 2 - (3,5 - di - tertiary - butyl - 2 - hydroxyphenyl) - 5 - chlorobenzotriazole.

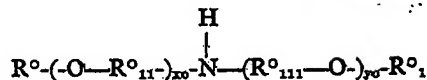
5. A composition as claimed in any one of the preceding claims wherein the anti-static agent comprises at least one compound which has one of the following structures:—



wherein R is a C_8 to C_{22} , inclusive, hydrocarbon radical, R' and R'' are the same or different and are C_1 to C_8 alkylene radicals, and x and y are the same or different whole numbers and each is 1 to 14, inclusive, the sum of $x+y$ is a whole number from 2 to 15; or:—



wherein R_1 is a C_7 to C_{21} , inclusive, hydrocarbon radical, R_1' and R_1'' are the same or different and are C_1 to C_8 alkylene radicals, and x_1 and y_1 are same or different whole numbers and each is 1 to 14, inclusive, and the sum of x_1+y_1 is a whole number from 2 to 15; or:—



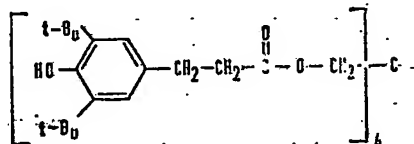
wherein R^o and R^o_1 are the same or different and each is H or a C_8 to C_{22} , inclusive, hydrocarbon radical, with the proviso that not more than one of R^o and R^o_1 is H; R^o_{11} and R^o_{111} are the same or different and are

C_1 to C_5 alkylene radicals, and x_0 and y_0 are the same or different whole numbers and each is 1 to 14 inclusive, and the sum of $x_0 + y_0$ is a whole number of from 2 to 15; and wherein all of the hydrocarbon and alkylene radicals are either substituted or unsubstituted.

6. A composition as claimed in claim 5 wherein the anti-static agent is N - (3 - dodecyloxy - 2 - hydroxypropyl) - ethanolamine.

7. A composition as claimed in any one of the preceding claims wherein the thermal stabilizer is octadecyl 3 - (3,5 - di - tertiary butyl - 4 - hydroxyphenyl) - propionate.

8. A composition as claimed in any one of claims 1 to 6 wherein the sterically hindered phenol is tetrakis[3 - (3,5 - ditertiary butyl - 4 - hydroxyphenyl) propionate methylene] - methane having the formula:



9. A composition as claimed in any one of the preceding claims comprising 45 to 85 weight per cent of a base resin of high density polyethylene or polypropylene, 5 to 45 weight per cent of filler, 3 to 15 weight per cent of an accommodation resin of low density polyethylene or ethylene copolymers, and wherein the amount of ultra-violet light stabilizer is from 0.2 to 2.0 weight per cent, the amount of anti-static agent is from 0.1 to 2.0 weight per cent and the amount of thermal stabilizer is from 0.02 to 1.0 weight per cent, with the proviso that the weight of the individual components of the composition are so selected that the total weight per cent is equal to 100.

10. A composition as claimed in claim 9 wherein the base polyolefin resin is high density polyethylene.

11. A composition as claimed in claim 10 wherein there is from 63 to 67 weight per cent of high density polyethylene.

12. A composition as claimed in any one of claims 9 to 11 wherein there is from 23 to 33 weight per cent of non-colloidal filler.

13. A composition as claimed in any one of claims 9 to 12 wherein the filler is calcium carbonate or titanium dioxide.

14. A composition as claimed in any one of claims 9 to 13 wherein the accommodation resin is present in an amount of from 5 to 7 weight per cent.

15. A composition as claimed in any one of claims 9 to 14 wherein the ultra-violet light

stabilizer is present in an amount of from 0.4 to 0.6 weight per cent.

16. A composition as claimed in any one of claims 9 to 15 wherein the anti-static agent is present in an amount of from 0.15 to 0.21 weight per cent.

17. A composition as claimed in any one of claims 9 to 16 wherein the thermal stabilizer is present in an amount of from 0.04 to 0.10 weight per cent.

18. A film or sheet made from the composition as claimed in any one of claims 1 to 8.

19. A film or sheet made from the composition as claimed in any one of claims 9 to 17.

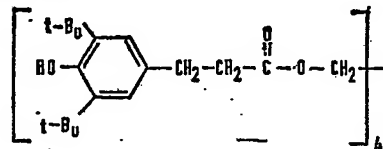
20. A process which comprises preparing a paper-like film from a polyolefin composition comprising a polyolefin and stabilizingly effective quantities of: an ultra-violet light stabilizer which comprises at least one organic compound which does not volatilize or decompose below 200°C. and is a 2 - hydroxybenzophenone or 2 - hydroxyphenyl - benzotriazole derivative as defined in claim 2; an anti-static agent which comprises at least one compound which does not volatilize or decompose below 200°C. and is an alkoxyated amide or amine which contains at least one saturated or unsaturated hydrocarbon group having from 7 to 22 carbon atoms and optionally bearing one or more substituents; and a thermal stabilizer which is at least one sterically hindered phenol which does not volatilize or decompose below 200°C.

21. A process as claimed in claim 20 in which said composition is based on high density polyethylene.

22. A process as claimed in claim 20 or claim 21 in which the ultra-violet light stabilizer is 2 - hydroxy - 4 - n - octoxybenzophenone or 2 - (3,5 - di - tertiary butyl - 2 - hydroxyphenyl) - 5 - chlorobenzotriazole.

23. A process as claimed in any one of claims 20 to 22 in which the anti-static agent comprises N - (3 - dodecyloxy - 2 - hydroxypropyl)ethanolamine.

24. A process as claimed in any one of claims 20 to 23 in which the thermal stabilizer comprises tetrakis [3-(3,5-di-tertiary butyl-4 - hydroxyphenyl) - propionate methylene] methane of the formula:—



25. A process for making a paper-like film substantially as hereinbefore described in any

one of Examples 4, 16, 17, 24, 25, 26, 32 or 33.

26. A paper-like film whenever produced by the process as claimed in any one of claims

5 20 to 25.

27. A polyolefin film substantially as hereinbefore described in any one of Examples 4, 16, 17, 24, 25, 26, 32 or 33.

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